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JAROSITE FORMATION IN THE URANIUM PROCESSING CIRCUIT OF DENISON MINES LIMITED, ELLIOT LAKE, ONTARIO

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JAROSITE FORMATION IN THE URANIUM PROCESSING CIRCUIT OF DENISON MINES LIMITED, ELLIOT LAKE, ONTARIO

by

J.E. Dutrizac*

ABSTRACT

Jarosite precipitation occurs in several parts of the uranium processing circuit of Denison Mines Limited, Elliot Lake, Ontario. Extensive precipitation of jarosite takes place in the filter cloth and on the drum face of the secondary drum filters, and this precipitation causes severe operating difficulties. Precipitation of jarosite is also observed in the ion exchange beads, but it is not known whether the jarosite is responsible for the observed decrease in resin efficiency. The resin beads are also rimmed with significant quantities of silica, lead, phosphate, sulphate, etc. which could be responsible for the fouling of the resin. In every instance, potassium jarosite, containing only minor amounts of sodium or ammonium, was the observed species; the potassium likely originates from the acid leaching of muscovite in the ore. Potential methods of avoiding the jarosite problem are discussed, but these may not be compatible with the overall process requirements.

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FORMATION DE JAROSITE DANS LE CIRCUIT DE TRAITEMENT DE L'URANIUM À LA DENISON MINES LIMITED, ELLIOT LAKE (ONTARIO)

par

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RÉSUMÉ

La formation de jarosite se produit dans plusieurs parties du circuit de traitement de l'uranium à la Denison Mines Limited, Elliot Lake (Ontario). Une précipitation importante de jarosite qui est la source de sérieuses difficultés opératoires se produit dans la toile filtrante et à la surface des tambours filtrants auxiliaires. La précipitation de jarosite est également observée sur les résines échangeuses d'ions mais on ignore si la jarosite est la cause de la diminution observée dans l'efficacité des résines. Les résines sont aussi encerclées de quantités importantes de silice, de plomb, de phosphate, de sulphate, etc. qui peuvent être une cause d'encrassement. Dans chaque cas, la jarosite de potassium à faible teneur en sodium ou en ammonium a été observée; le potassium provient vraisemblablement de la lixiviation à l'acide de la muscovite contenue dans le minerai. Le rapport présente des méthodes possibles pour résoudre le problème que pose la jarosite bien qu'il est possible que celles-ci ne soient pas compatibles avec les exigences globales du procédé.

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INTRODUCTION

Denison Mines Limited operates a 15,000 t/d uranium mining-processing facility in the Elliot Lake area of Ontario (1). The ore is mined entirely by underground methods, and is transferred to the surface where it is milled and then leached at 75°C in concentrated sulphuric acid (~70 g/L H_2SO_4). Hot, concentrated acid is required to achieve a significant degree of uranium recovery from the brannerite mineralization which is a significant factor in the Denison ores. Sodium chlorate is added, as an oxidant, in the leaching pachucas. After leaching, excess free acid is neutralized with lime to yield a final pH of 1.8-2.0. The limed slurry is thickened and the solution overflow is forwarded for uranium recovery. The thickener underflow is filtered, and the primary filter cake is repulped with water and filtered a second time on a drum filter, with water washing, prior to tailings discharge. At the Denison operation, uranium is recovered by ion exchange using both older moving bed ion exchange equipment (6,400 L/min) and newer stationary bed apparatus (8,200 L/min). The uranium is stripped with nitrate ion and is subsequently precipitated with ammonia to produce an ammonium yellow cake.

As might be expected from an operation which employs lime neutralization of relatively concentrated sulphuric acid media, extensive gypsum scaling is not unknown in the Denison mill. In certain parts of the plant, however, scaling and/or fouling problems exist which do not seem to be caused by gypsum but appear to be related to some iron compound or compounds. One area of particular concern is the secondary drum filters where an impervious scale buildup occurs in the filter cloth and on the drum face itself. This requires extensive maintenance to grind and/or chip off the scale and also necessitates the periodic replacement of filter cloths and parts of the drum filter piping. The other major area of concern is the ion exchange operation

where fouling of the resin occurs together with extensive cracking of the resin beads. This fouling results in increased regeneration costs for the company.

Because the troublesome iron compound was thought to be a jarosite-type compound ($MFe_3(SO_4)_2(OH)_6$ where M = K, Na, NH_4, H_3O, $\frac{1}{2}Pb^{2+}$, etc.) and because of CANMET's experience with jarosite precipitation (2,3), Denison Mines requested that CANMET examine some of their mill products to see whether jarosites were actually involved and to offer throughts on how the jarosite problem might be avoided. This report summarizes the results obtained on the limited number of samples provided by Denison Mines.

EXPERIMENTAL

Six samples were provided by Denison Mines from the following parts of their operation.

1 - Several pieces of fist-size rock from the underground operation. The rocks were covered by a yellow clay-like layer thought to be jarosite.

2 - Clarified leach recycle solution from the leaching stage prior to liming; a white precipitate had formed during transport of this solution.

3 - Clarified pregnant solution from the leaching stage after liming; a white precipitate was also present in this solution.

4 - Secondary drum filter buildup that was ground and/or chipped from the face of the filter. This sample consisted of flakes of a hard yellow-brown material which was also believed to be jarosite.

5 - Moving resin bed ion exchange gravel that is used to support the resin itself. The gravel consists of large (several cm) pebbles with adhering resin beads.

6 - Dumped resin beads from the fixed bed ion exchange circuit. The beads were coated with some sort of scale, and many beads were broken.

The pieces of rock were examined with a binocular microscope and select samples of the yellow coating were subjected to X-ray diffraction analysis using 57.3 mm Debye-Scherrer cameras and CoK_α radiation.

The two solution samples were filtered to remove the white precipitate which was identified by X-ray diffraction analysis. The pH of the filtered solution was measured, iron was determined by traditional dichromate titration, sulphate was done by barium sulphate precipitation and other metals were analyzed by atomic absorption spectroscopy. To determine the potential for the precipitation of jarosite-type compounds, both filtered solutions were heated to 97°C for 24 h with stirring. Previous work has shown that such conditions are near-optimum for the precipitation of jarosite (2,3). Any precipitates were subjected to chemical and X-ray diffraction analyses.

A portion of the secondary drum filter buildup was dried, ground and then subjected to X-ray diffraction and chemical analyses. Several of the original unground flakes were mounted in epoxy, polished and examined by a scanning electron microscope (SEM) with energy dispersive X-ray analyzer (EDX) and backscattered electron imagery. Efforts were also made to analyze quantitatively the jarosite grains found in this material. The analyses were done with a MAC 400 electron microprobe, and the data were corrected using a modified version of the EMPADR VII computer program.

The moving resin bed ion exchange gravel was water-washed on a 20 mesh screen to separate the resin beads and other fine material from the coarse sterile gravel. The -20 mesh fraction was subsequently wet screened on a 150 mesh screen and the -150 mesh fraction was collected, dried and subjected to analysis. The -20 +150 mesh fraction consisted almost entirely of resin beads.

The resin beads from the screening of the moving resin bed gravel and from the dumped resin from the fixed bed circuit were leached in a small amount of concentrated hydrochloric acid and the leach solution was analyzed for K, Fe, etc. to ascertain whether the resin beads contained any jarosite. In addition, the beads from the dumped resin were subjected to SEM-EDX analysis to try to determine the causes for the observed resin fouling. The microscopic analytical techniques employed were discussed above.

RESULTS AND DISCUSSION

1 - Mine Rocks

Careful microscopic examination of the mine rocks showed that the yellow clay-like coating consisted mostly of fine, glassy quartz grains and tiny flakes of mica. The yellow colouring agent was present only in small amounts; consequently, the clay-like consistency of the coating must be due to the fine-grained quartz and mica. X-ray diffraction analysis of various samples of the coating indicated major quartz and muscovite (mica) together with traces of K-jarosite ($KFe_3(SO_4)_2(OH)_6$) and rutile (TiO_2). Although jarosite is clearly forming in the mine environment and is likely responsible for the yellow colour of the coatings, the amounts of jarosite are minor and its precipitation cannot be considered a serious problem.

2 - Solution Samples

The white precipitate present in both solution samples was shown by X-ray diffraction analysis to be gypsum ($CaSO_4 \cdot 2H_2O$).

The analyses of the two as-received solutions after removal of the gypsum are presented below.

	pH	Fe^{3+} (g/L)	Fe^{2+} (g/L)	K (g/L)	Na (g/L)	NH_4 (g/L)	Al (g/L)
Leach recycle solution	0.066	1.12	4.19	1.13	0.42	0.44	3.12
Clarified pregnant solution	1.84	0.28	1.12	0.37	0.14	0.16	0.59

Heating of the leach recycle solution to 97°C for 24 h resulted in no precipitation whatsoever. By contrast, heating the clarified pregnant solution to 97°C resulted in the precipitation of K-jarosite which had the following composition, in wt.%: K 6.56, Na 0.09, NH_4 0.037, Fe 20.60, Al 6.36, SO_4 40.75.

The leach recycle solution contains all the ionic constituents necessary to form a jarosite-type precipitate (K, Na, Fe^{3+}, SO_4, etc.) but the acidity is too high for this to happen, even when the solution is heated to 97°C, considerably higher than the 75°C plant leaching temperature. Liming of the leach solution raises the pH to ∿1.8 and this pH is nearly ideal for jarosite formation (2). Judging from the significant reductions in the concentrations of K, Na, Fe^{3+} and Al after liming of the leaching solution, significant amounts of an aluminum-bearing K-jarosite have been, or are being, precipitated in this part of the circuit. Such a conclusion is supported by the observed precipitation of additional aluminum-bearing K-jarosite on heating the clarified pregnant solution to 97°C. Potassium is the major alkali in solution, and it almost certainly originates from the concentrated acid attack of the muscovite ($KAl_2(Si_3Al)O_{10}(OH,F)_2$).

Furthermore, potassium is selectively concentrated into jarosite-type compounds at the expense of either sodium or ammonium, and this is reflected in the composition of the jarosite formed on heating:

$$(K_{0.79}Na_{0.02}NH_4{}_{0.01}H_3O_{0.18})_{1.00}(Fe_{1.73}Al_{1.11})_{2.84}(SO_4)_{2.00}(OH)_6$$

Hence, efforts to eliminate sodium (e.g., sodium chlorate as an oxidant) or ammonium (e.g., ammonia for uranium precipitation) from the circuit will likely have a negligible effect on the amount or composition of the jarosite formed. Potassium could likely be reduced by lowering the temperature and H_2SO_4 concentration of the leaching step, but this will certainly result in unacceptable uranium extractions. Prior flotation of the mica might eliminate the source of the potassium (and aluminum?), but such an option would require considerable process development.

3 - Drum Filter Buildup

X-ray diffraction analysis of the secondary drum filter buildup showed it to consist of jarosite and minor quartz. Chemical analysis of the acid soluble part of the bulk material gave, in wt.%: K 4.80, Na 0.03, NH_4 0.052, Fe 22.65, Al 1.70, SO_4 29.54. The total is low relative to the jarosite composition because of the presence of insoluble substances such as quartz. The analysis of the bulk sample suggests a jarosite composition of:

$$(K_{0.80}Na_{0.01}NH_4{}_{0.02}H_3O_{0.17})_{1.00}(Fe_{2.65}Al_{0.41})_{3.06}(SO_4)_{2.00}(OH)_6$$

The suggested composition is similar to that of the jarosite formed by heating the clarified pregnant solution except for the high Fe + Al total and the Fe/Al ratio. Both these anomalies may be related to the presence of minor amounts of pyrite in the sample (seen optically but not detected by X-ray diffraction analysis). The pyrite would contribute iron causing both a high iron content and an elevated Fe/Al ratio.

Figure 1 presents a general view of one of the scale fragments that clearly illustrates the layered texture expected for the repetitive buildup of a scale. Although considerable porosity exists, the scale is generally compact and could conceivably plug a filter. The light grey phase which constitutes the bulk of the sample is K-jarosite, the medium grey phase is a potassium aluminum silicate (likely muscovite), the dark almost black grains are quartz, and the white specks are pyrite. Figure 2 illustrates the structure of the scale in greater detail. Again, the major light grey phase is K-jarosite, the medium and dark grey phases are muscovite and quartz and the white specks are pyrite. The pyrite grains are only a few microns in size, and the plate-like texture of the mica grains is now evident. The jarosite crystals are very small and are barely resolved even at the high magnification used. Although the jarosite crystals are small, an effort was made to analyze this phase using the electron microprobe. The average composition found was, in wt.%: K 5.9, Pb 2.5, Fe 31.2, SO_4 36.8. The presence of lead, which was not sought in the bulk analyses was somewhat unexpected. The lead is likely radiogenic in origin and almost certainly substitutes for K in the jarosite structure (3,4). Discrete $PbSO_4$ grains, even tiny grains, are quite evident on the SEM.

That jarosite is observed during filtration suggests that the filtration operation is being carried out while the slurry is warm and while jarosite is still precipitating in the limed slurry. Two potential methods of resolving this jarosite precipitation problem seem possible. In the first case, the limed slurry could be kept hot until all the jarosite had precipitated, and then the filtration could be carried out. At the 70°C operating temperature, however, the retention time at temperature to achieve complete jarosite precipitation could be up to two days. In the

second case, the slurry would be chilled to <25°C to prevent, or greatly slow, the rate of jarosite formation. The extent to which either of these approaches is being done, or could be done, is not known. It is reported that the formation of jarosite is somewhat erratic, and this may indicate that either or both of the above conditions are now being inadvertently satisfied some of the time.

4 - Ion Exchange Resins

X-ray diffraction analysis of the -150 mesh fraction from the moving resin bed ion exchange gravel indicated quartz and K-jarosite together with a trace of $PbSO_4$ which likely originated from the acid attack of radiogenic lead. X-ray diffraction analysis of a crushed bead from the fixed bed resin indicated an amorphous phase, presumably the resin itself. Thin light brown, dark brown or yellowish coatings on the dumped fixed bed resin were shown to consist of jarosite and quartz. The brownish coloration, however, also suggests the presence of amorphous iron compounds not detectable by X-ray diffraction analysis.

Examination of the dumped fixed bed resin beads by SEM-EDX failed to detect any precipitated scale on the surface of the beads, but an impregnation or concentration of elements in the outer parts of the resin beads was observed. Sulphate was evident throughout the beads, but iron, titanium, thorium, phosphate and chloride were generally concentrated on the periphery of the grains. One bead had a chlorine-rich core. A lead-rich phase was observed impregnating the extreme outer portion of most of the beads. The outer surface areas of the resin beads were also generally enriched in Si, likely present as colloidal silica or extremely fine quartz particles. Figure 3 presents a general view of the resin beads taken using all back-

scattered electrons. The general concentration of various elements on the outer part of the resin beads is evident as lighter rims present on most of the beads. The lead phase is the outermost white rim.

Figure 4a shows the detailed structure of four of the resin beads, one of which has been broken and another of which shows the development of radial cracks. As the lighter rims of these backscattered electron micrographs indicate, there has been a significant concentration of heavier elements in the outer portions of the beads. The thin white band at the extreme outer edge of the beads is due to an enrichment of lead. From the tests done, it is impossible to state whether the lead is adsorbed on the resin or is present as very fine particles of $PbSO_4$ or Pb-bearing jarosite. Since both iron and sulphate are also concentrated in the outer portions of the beads, any of the three occurrences is possible. Figure 4a shows the SKα X-ray map of these beads, and it is evident that significant amounts of sulphate have been incorporated into the resin. Figure 4b illustrates the corresponding FeKα X-ray map, and the concentration of iron around the rim of the beads is apparent. Other X-ray mapping studies have illustrated the concentration of several elements in the rims of the resin beads. These species include phosphate, silica, thorium and uranium. Presumably the concentration of these elements on the periphery of the beads reduces the resin's capacity for uranium. From the limited amount of work done in this preliminary study, however, it is not clear which elements are most deleterious or, in fact, if the presence of these elements is really the cause of the resin fouling.

The SEM-EDX photomicrographs suggest that both Fe^{3+} and SO_4^{2-} are concentrated in the outer portions of the resin, but clearly both anions and cations cannot be adsorbed onto the strong base anion exchange resin used

at the Denison operation. Jarosite was identified by X-ray diffraction analysis of the surface layers of the beads, and this may indicate the precipitation of very small jarosite particles in the pores of the resin. Some support for this mechanism comes from the leaching tests where it was observed that the molar ratio of Fe:K leached from the beads was consistently ~4.4, a value not too dissimilar from the 3.7 molar ratio determined by microprobe for the jarosite in the drum filter buildup.

Although the presence of fine jarosite precipitates in the rims of the resin beads is inferred (but not proved), jarosite precipitation has definitely occurred in a number of the cracked resin beads. A considerable number of dark brown or orange-brown broken resin beads were present in the dumped fixed bed resin and these were also examined by SEM-EDX. Figure 5 presents a general view of several of these fractured beads. The fractured resin beads (light to dark grey) are themselves badly cracked and many of the fissures have been filled with a second phase (white). SEM-EDX analysis of the fracture fillings indicated major potassium, iron and sulphate, suggesting strongly the presence of K-jarosite. Trace amounts of lead are also present, and this likely indicates that the K-jarosite is slightly lead-bearing (4). Within the context of this limited investigation, it is not known whether the formation of the K-jarosite has caused the fracturing or whether the jarosite has simply formed in pre-existing cracks. That many of the cracks are jarosite-free (see also Fig. 4a) suggests the jarosite is simply a fracture filling.

At this point it is not known for certain whether the presence of jarosite in the resin beads is responsible for the resin fouling/deterioration. So many elements are concentrated in the rims of the beads that any one of them could be responsible for the reduced resin efficiency. Since the leach

solutions will always contain Fe^{3+} and SO_4, the prevention of jarosite formation would require close control over the amount of potassium. This will be extremely difficult to achieve given the leaching conditions used. Again, early removal of the mica from the ground ore might be one method of avoiding dissolved potassium and, consequently, jarosite formation; mica removal might also eliminate much of the dissolved silica as well. Another approach would be to reduce all the iron to the ferrous state which does not form jarosite-type compounds. This approach would clearly be very costly, both for reagents and for the equipment to keep the iron in the Fe^{2+} state during ion exchange.

CONCLUSIONS

The somewhat limited amount of test work done on the six samples provided by Denison Mines Limited has shown the following points concerning jarosite precipitation in their circuit.

1 - A small amount of K-jarosite forms on mine rocks in the underground environment. The yellow clay-like coating on the rocks consists mostly of fine particles of quartz and muscovite, coloured yellow by minor quantities of the jarosite.

2 - The actual leaching solutions contain the elements necessary for jarosite precipitation, but the solution is too acidic for this to occur. Once the solution is limed to pH $\sim$1.8, K-jarosite precipitation readily occurs at $\sim 70^{\circ}C$.

3 - The scale buildup on the secondary drum filters consists mostly of K-jarosite containing only minor amounts of Na or NH_4 substituting for the potassium.

4 - An enrichment of potassium, lead, iron and sulphate occurs in the rims of the ion exchange resin beads, but it is not known whether these species are present as small jarosite grains or simply as sorbed ions. Several other species such as phosphate, silica and thorium are also concentrated in the rims of the beads.

5 - K-jarosite precipitates were widely found in the cracks of broken resin beads. It is suspected that the jarosite is simply a fracture filling and that its precipitation is not responsible for the disintegration of the beads.

Several potential methods exist to prevent or minimize the formation of jarosite in Denison's uranium processing circuit. Many of the suggested methods will likely prove to be either too expensive or not compatible with the existing operation. The elimination of the muscovite from the ore, say by flotation, might be an attractive option. Muscovite elimination would likely reduce the input of potassium, iron and soluble silica into the processing solutions with concomitant reductions in jarosite formation and resin bead fouling.

ACKNOWLEDGEMENTS

SEM-EDX analyses were done by D.R. Owens.

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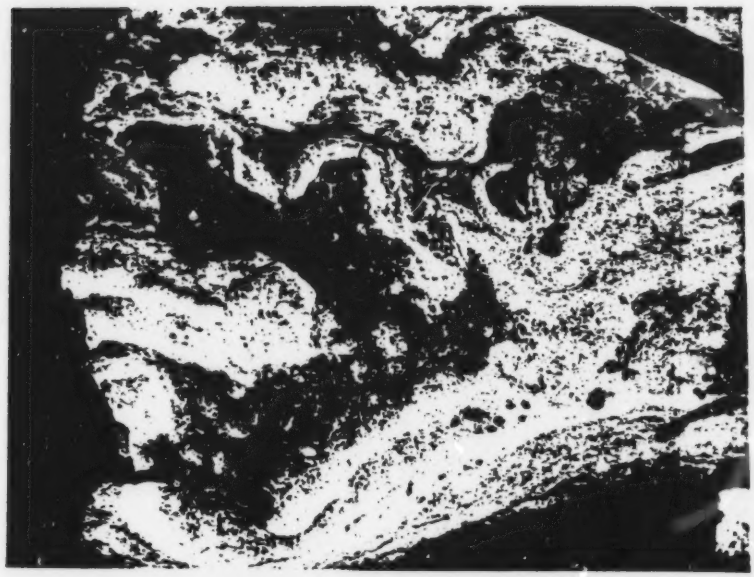

Fig. 1 - Backscattered electron micrograph showing the texture of the secondary drum filter buildup. The light grey phase is K-jarosite and the other phases are identified in the text.

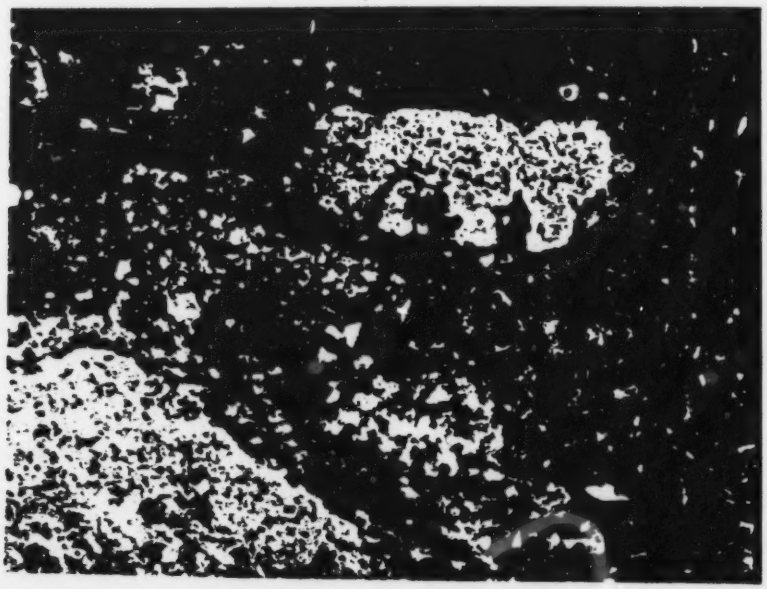

Fig. 2 - Backscattered electron micrograph showing the phases present in the secondary drum filter buildup. The light grey phase is K-jarosite and the other phases are identified in the text.

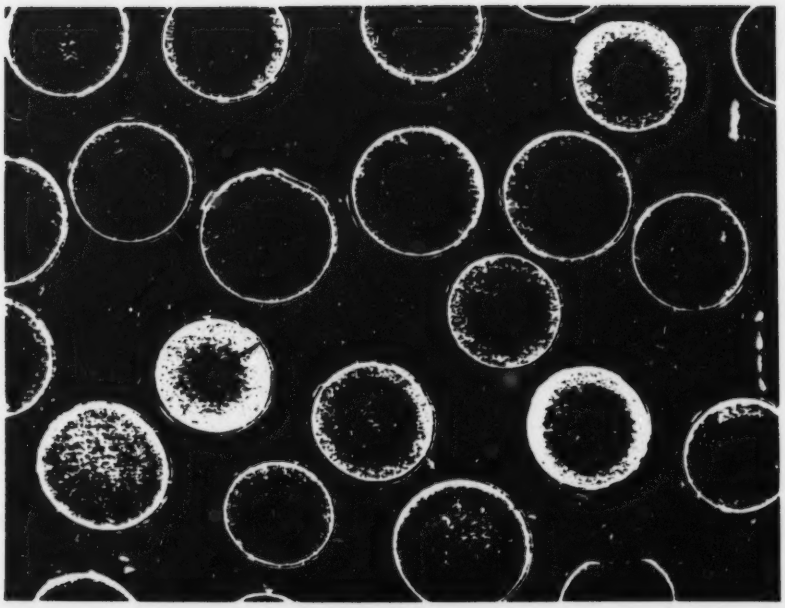

Fig. 3 - Backscattered electron micrograph of the resin beads in the dumped fixed bed. The light rims indicate a concentration of elements on the outer parts of the beads; the outermost white rim is a lead-rich phase.

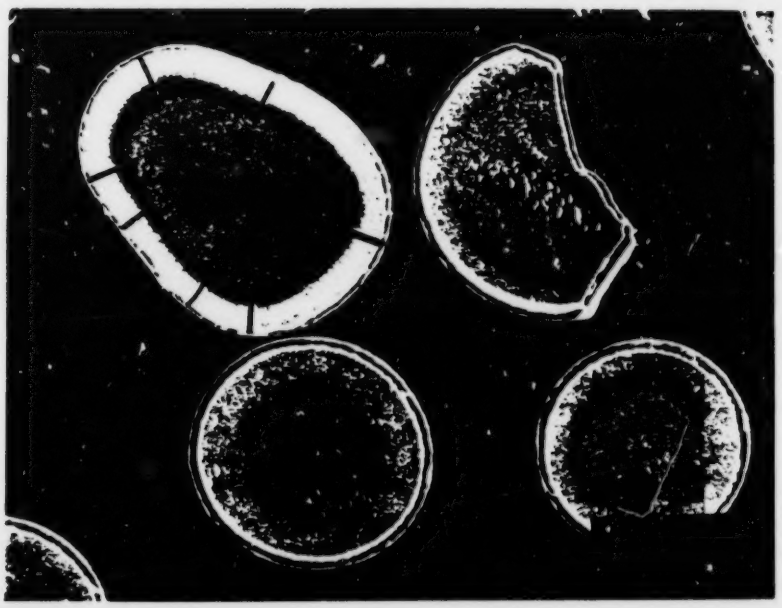

Fig. 4a - Backscattered electron micrograph of four resin beads showing a concentration of elements in the rims (white and light grey).

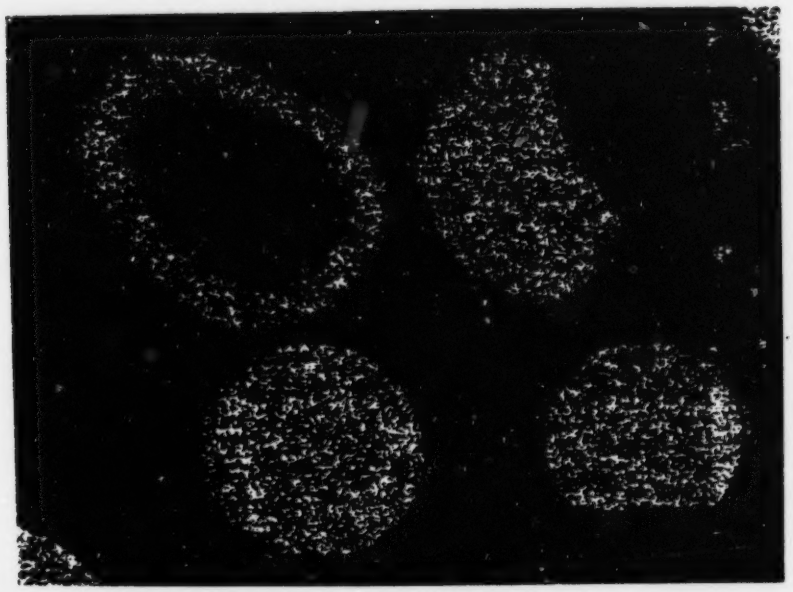

Fig. 4b - Sulphur Kα X-ray map showing the relative distribution of sulphur (sulphate) in the resin beads of Fig. 4a.

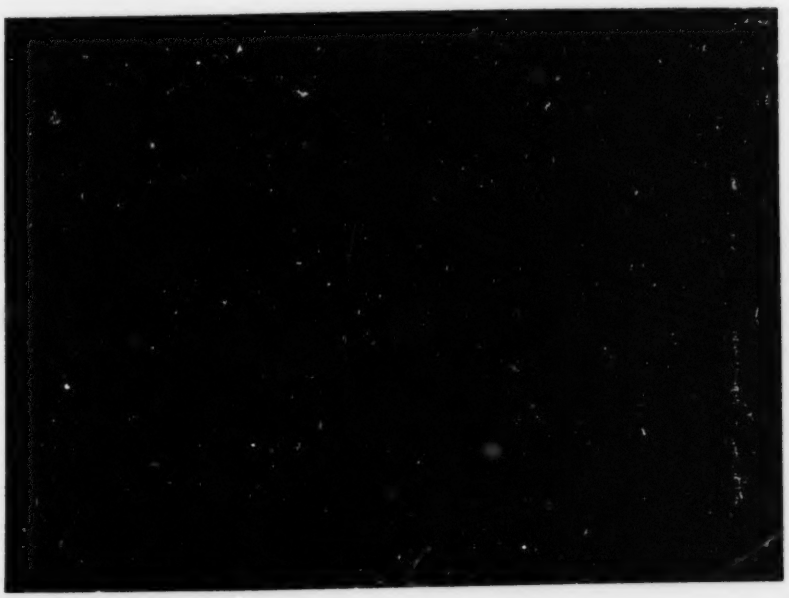

Fig. 4c - Iron Kα X-ray map showing the relative distribution of iron in the resin beads of Fig. 4a.

Fig. 5 - Backscattered electron micrograph of fractured resin beads (grey) from the fixed bed. The white phase is K-jarosite filling fractures in the cracked resin beads.